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THE USE OF SULFOLANE IN THE PHOTOMETRIC DETERMINATION OF SILICON

A THESIS

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THE USE OF SULFOLANE IN THE

PHOTOMETRIC DETERMINATION OF SILICON

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SUMMARY

The subject of this investigation has been the application of sulfolane in the development of an improved method for the determination of silicon as the silicomolybdic acid complex. The use of the silicomolybdic acid complex for analytical purposes has long been a difficult problem due to the complex nature of the reaction of the silicate and molybdate ions at varying acidity. Strickland's now famous work helped to improve the situation with the discovery that the silicomolybdic acid exists as two isomers: the alpha acid formed in mildly acidic solutions and the beta acid formed in strongly acidic solutions. The unstable β-form has twice the absorptivity at 400 nm of the α-form, and spontaneously converts to the α-acid. Most authors have forsaken the β-acid as a means of determining silicon because of its instability and have used the lower absorbing α-form.

Thus search for a reagent which would enhance the color of the α-silicomolybdic acid was warranted. Little work has involved adding a water-miscible enhancing agent directly to the α-silicomolybdic acid solution, and the results are at most not spectacular.

Because sulfolane has shown to enhance the color of several metal complexes, it was applied to the silicomolybdic acid system as a possible water-miscible enhancing agent. Investigations indeed showed that sulfolane enhances the color of the α-acid significantly, but only slightly enhances the color of the β-form. Further study, however, indicated that sulfolane stabilizes the β-silicomolybdic acid. Because

the stabilized β-form was found to still have a higher absorptivity than the enhanced α-form, an analytical method was developed in this study for the determination of silicon as the sulfolane-β-silicomolybdic acid.

CHAPTER I

INTRODUCTION

The ultimate purpose of this work is to establish an improved photometric method for the analytical determination of silicon as the silicomolybdic acid complex.

Photometry is based on the Lambert-Beer (1) Law: The relationship between the radiant power of the incident and transmitted light as a function of both the length of the light path and of the concentration of the absorbing species in the solution. This relationship is conveniently expressed mathematically as:

$$\text{Log } \frac{1}{T} = A = abc \qquad (1)$$

where:

T = Transmittance; the ratio of the radiant power P transmitted by a sample to the radiant power P_o incident on the sample.

A = Absorbance; the negative logarithm (to the base 10) of the transmittance.

a = Absorptivity; a measure of the ability of a material to absorb light.

b = Path length; usually expressed in centimeters.

c = Concentration; usually expressed in terms of grams per liter or moles per liter.

The employment of techniques to extend the sensitivity of an established photometric method by increasing the absorbance of the sample solution is analytically of value because the limit of determination can often be decreased. From equation (1) it is apparent that the value of the absorbance and therefore the sensitivity of the method can be altered by changing the value of one or more of the parameters: a, b, c. Thus, an increase in the value of one or more of these parameters could increase the absorbance and be of value in increasing the sensitivity of the photometric method.

One means of increasing the absorbance of a solution is by extending the path length b. Barnes (2) has constructed a spectrophotometer accomodating a much longer cell than found in conventional instruments. Experiments by Barnes have shown that the limit of determination of many types of photometric methods can be extended utilizing this instrument.

Another approach to increasing sensitivity is through enrichment of the material of interest with extraction into a water immiscible organic solvent of a smaller volume than that of the original solution. Extractions not only provide for enrichment but also have the added advantage of performing a separation from interferences. Furthermore, the extraction can be effected in such a way that a compound results that is of a higher absorptivity than the one originally present. This leads into the third approach to increasing sensitivity, namely by operating with an increase in absorptivity, a, the third parameter in the Lambert-Beer Law. Such an increase may be achieved due to some beneficial influence of the solvent employed in the initial

formation of the complex or adduct, or for already existing complexes. This modus of operation was used in the present work for the silicon determination.

The separation of silicomolybdic acid from the other heteropolymolybdates (especially arsenic and phosphorous) by extraction from an aqueous solution into various organic solvents has repeatedly been investigated. Keggin (3) stated that oxygen-containing organic materials are good solvents for heteropolymolybdates, while carbon disulfide, carbon tetrachloride, chloroform, benzene, toluene, and other hydrocarbons are not.

In addition to separating the silicomolybdic acid from the other heteropolymolybdates and effectively increasing the concentration of the complex due to the reduced volume of the organic phase, extraction with certain organic solvents has shown the previously mentioned enhancement of the absorptivity of the silicomolybdic acid complex. Mellon (4) and Souchay (5) performed rather exhaustive studies of the extraction behavior of the silicomolybdic acid with respect to many types of organic solvents and gave extensive discussions of the extraction efficiencies and enhancing abilities. Andersson (6) reported n-butanol to show the highest selectivity for the silicomolybdic acid complex and to exert the greatest enhancing effect.

Although much work has been done to increase the absorptivity of the silicomolybdic acid complex by extraction with certain organic solvents, very little attention has been paid to the possibility of adding a water soluble enhancing agent directly to the silicomolybdic acid solution. Fujinaga (7) reported that dioxane, methanol, ethanol,

and acetonitrile, have some enhancing effect upon the heteropolymolybdates, and concluded that tetrahydrofuran showed the most pronounced effect. Chalmers (8) and Halasz (9) have reported great success in using acetone as an enhancing agent for the silicomolybdic acid complex. There are, however, disadvantages in employing this compound: (1) Acetone is extremely volatile and changes in solution volume, due to evaporation, can lead to erroneous results; (2) Turbidity develops when acetone is added to extremely acidic solutions, and this is intolerable for photometric methods. Thus, further search for enhancing agents was warranted.

Solfolane (tetrahydrothiophene - 1, 1 - dioxide) was known (10) as a good water miscible solvent for various metal salts. When investigating this property for other purposes, considerable color enhancement of the blue of the thiocyanato complex of cobolt was noted (2). Expansion of the investigation to other metal thiocyanates was made, but the effects were, by far, less than with cobolt. However, an interesting situation prevailed for silicomolybdic acid and therefore the system was subjected to closer study.

It was found that the drawbacks mentioned for acetone do not exist for sulfolane.

CHAPTER II

THE SILICATE-MOLYBDATE SYSTEM

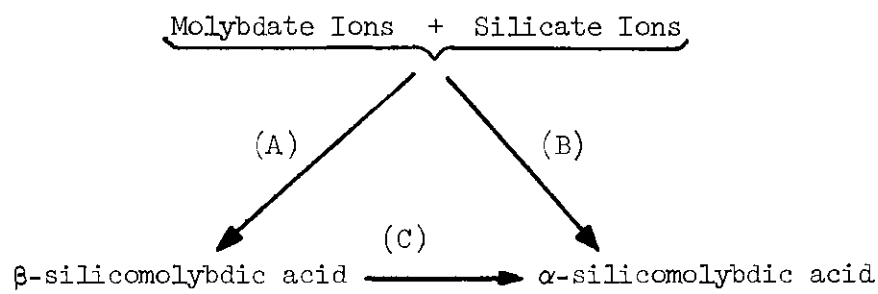
In 1898, Jolles (11) discovered that the silicate and molybdate ions react in acidic media to form the yellow silicomolybdic acid complex. Since then much work has been devoted to using this method for the determination of silicon. The fact that this method is so often mentioned as a standard method of analysis for silicon (12) gives evidence to its wide-spread usage. It was not until about 1930, when more advanced spectrophotometers became available, that more thorough investigations could be undertaken. Mullin (13) and Mellon (14) give extensive references to these studies and summaries of much of the initial work.

The earlier literature concerning the analysis of silicon via the silicomolybdic acid contains many different methods with standardized conditions for various types of samples. However, most of these conditions were obtained empirically and little was known concerning the reaction between the silicate and the molydate ions. It is common knowledge that the formation of the silicomolybdic acid is dependent upon pH, time, and the presence of other material in the solution. Most of the earlier investigations of a fundamental nature were designed to optimize these conditions. The approach was strictly empirical with no consideration given to any theoretical concepts. A great variety of conflicting statements was published, which is of no surprise

considering the complexity of the situation at hand. While strict empiricism is not necessarily a hindrance of a fine working analytical method, the lack of knowledge of basic facts was very detrimental when modifications of procedures became necessary, or in cases where sample composition and silica content varied.

The confusion existing with regard to contradictory results reported by authors for methods of analysis employing the silicomolybdic acid complex was resolved by Strickland's (15) now famous investigation. Strickland's discovery that the silicomolybdic acid complex can exist in two forms was of considerable importance in establishing reliable methods of analysis. These two isomers were correspondingly named by Strickland the alpha and beta silicomolybdic acid.

Strickland (15) has found that the α-silicomolybdic acid complex is formed in a mildly acidic solution when the $^{H+}/_{Mo}$ ratio is less than 1.5. The β-silicomolybdic acid is formed in strongly acidic solutions when the $^{H+}/_{Mo}$ ratio is greater than 3.0. The α acid is the thermodynamically stable form; the unstable β acid spontaneously converts to the α form. Andersson (16) explained the mechanism of formation of the α- and β-silicomolybdic acid by a simplified scheme of transition paths:



(2)

Both Andersson (16) and Strickland (15) believed that in all cases the final α-silicomolybdic acid is obtained via the originally formed β-silicomolybdic acid, and then through conversion to the α-acid according to Path C. Neither author found evidence of a direct formation via Path B. Strickland reports that the $^{H+}/_{Mo}$ ratio actually affects the degree of polymerization of the molybdate ion. Variation in the degree of this polymerization with changing acidity is given as the reason why the formation of the α and β-silicomolybdic acid is pH dependent.

Ringbom (17) also felt that the two forms of the silicomolybdic acid complex are connected with the different types of polynuclear molybdate ions which are formed at various acidities. At a pH greater than 6.5, the MoO_4^{-2} ion is stable. At a pH of 4.5, the paramolybdate ion ($Mo_7O_{24}^{-6}$) is formed. The species is transformed to the octamolybdate ion ($Mo_8O_{26}^{-4}$) when the pH is lowered to less than 2.5.

Ringbom observed that in strongly acidic solutions (pH ≤ 2.0) the reaction between the silicate and molybdate ions produces an initially intense color which gradually fades and reaches a constant level. In the pH range of 2.5 - 3.5, the reaction between the silicate and molybdate ions produces a color which, within a short period of time, attains a constant intensity. Above pH of 4.0, the reaction produces a color which gradually becomes more intense. From these results Ringbom concluded that the α-silicomolybdic acid is formed from the paramolybdate ion in the pH range of 2.5 - 3.5. It was hypothesized that the β silicomolybdic acid was formed from the octamolybdate ion at a pH less than 2.0. In the pH range of 4.0 - 6.0, the reaction between the silicate

and molybdate ion is incomplete.

Chalmers (8) disputed Strickland's and Ringbom's claim that the pH dependence of formation for the two forms of the silicomolybdic acid is due to the varying degree of polymerization of the molybdate ion. He stated that in order for the molybdate ions to be of different composition in the α and β forms, an alteration in the charge per molybdenum atom is required. However, this is contrary to the experimentally established fact that the empirical formulae for the two forms are identical. Keggin (3, 18) has established the empirical formula of the silicomolybdic acid to be:

$$H_4SiMo_{12}O_{40} \cdot 24H_2O$$

After preparation of the quinoline salt, gravimetric analysis indicated that the molybdenum and silicon content of the α- and β-forms are identical. For structural evaluations, e.g. by X-ray powder analysis, only the α-silicomolybdic acid can be obtained as a solid. The fact that the β-form does not exist in the solid state is felt to be due to its instability.

Chalmers has attempted to explain the α to β transition by utilizing the Keggin structure (3) for the α-silicomolybdic acid (See Figure 1; where each dot represents a molybdenum atom). The α to β transition is hypothesized to be a structural change in the molecule involving the rotation through 60° of molybdenum atoms 1, 2, and 3 of a of Figure 1. This involves a change in symmetry from hexagonal to cubic and causes the breakage and reformation of six oxygen-

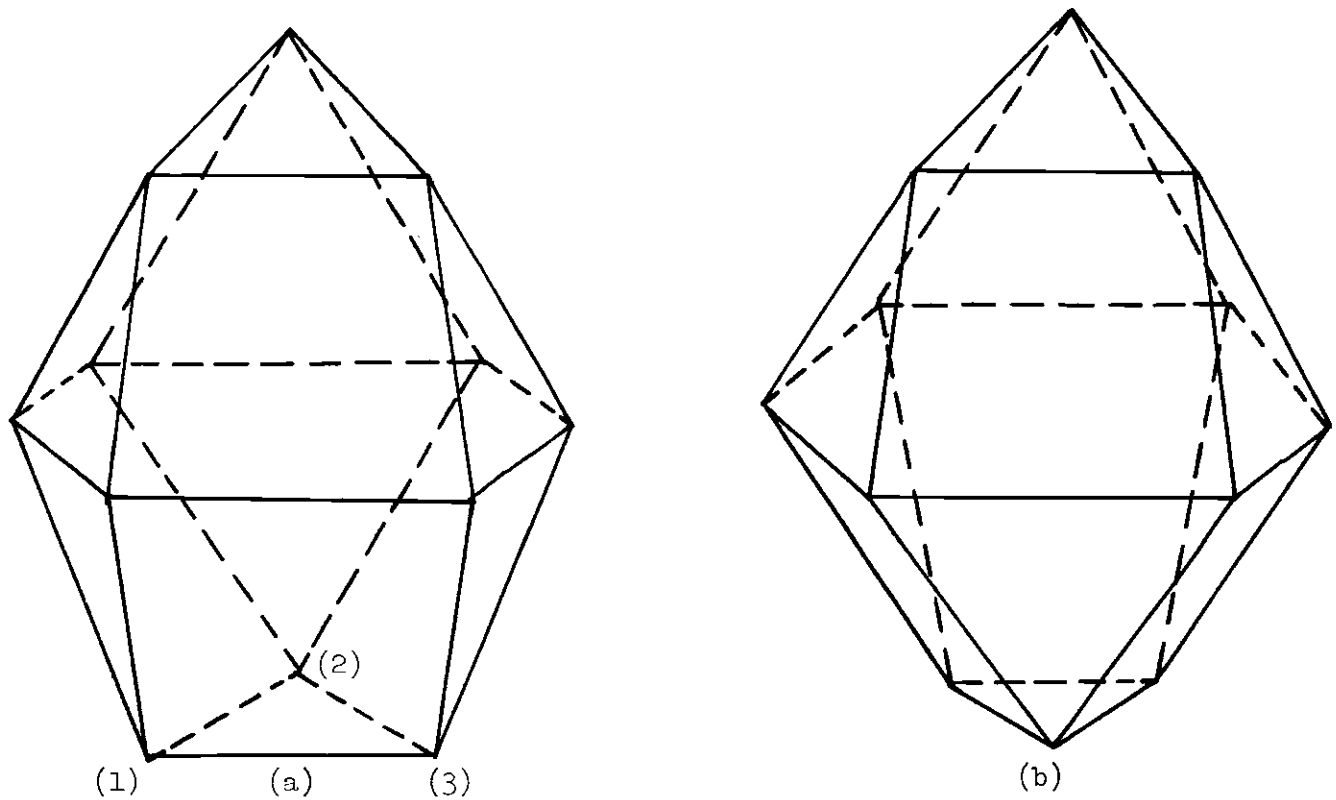


Figure 1. Proposed Structures of α and β Silicomolybdic Acid

(a) Chalmers' Proposed Structure for β-Acid

(b) Keggin's Proposed Structure for α-Acid

molybdenum bonds. Chalmers further suggests that the β-silicomolybdic acid might then convert to the α-form by a mechanism of water molecules bridging the singly coordinated oxygens of the molybdenum atoms. It was further hypothesized that if polar organic molecules of the right length were introduced to displace the water molecules around the molybdate ion, the β-form would be stabilized and be effectively blocked from transition to the α-form.

In addition to the many proposed theories available for explaning the considerable disagreement with regard to why certain water miscible organic solvents enhance the color of the silicomolybdic acid complex, Chalmers (8) has found that the absorptivities of the silicomolybdic acid complex in aqueous acetone and in an ether solution are identical. This and other information led Chalmers and Mellon (4) to the conclusion that the water molecules of the solvation sheath are replaced by polar organic molecules of the right length. The change in the electronic configuration of the silicomolybdic acid molecule due to the alteration of the solvation sheath was concluded to be the reason why some water miscible organic solvents enhance the solution color of the silicomolybdic acid.

If the conversion according to Path C is given enough time to go to completion, a stable yellow color is obtained. The conversion of the β to the α form is quite slow, but the reaction rate can be increased by addition of sodium chloride or by heating the solution on a steam bath. The β to α transition can be followed by observing the absorbance versus time change as shown in Figure 2. After about twenty hours have elapsed since the initial formation of the β-

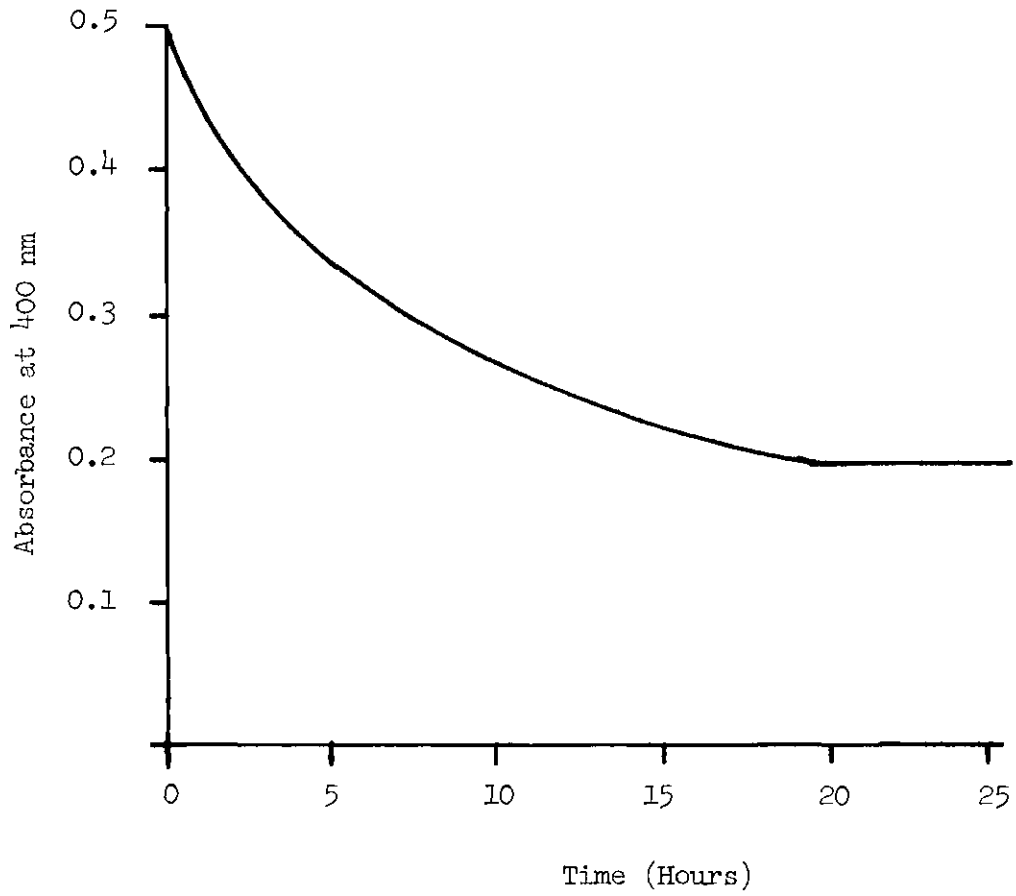


Figure 2. Absorbance at 400 nm of 2.3×10^{-4} F Silicomolybdic Acid as a Function of Time

silicomolybdic acid, the absorbance reaches a constant value, indicating the conversion to α-silicomolybdic acid being complete. The absorbance at 400 nm of the α-silicomolybdic acid is approximately one-half that of the β-silicomolybidc acid.

The two forms can be distinguished photometrically by their absorption spectra. Spectra obtained in this laboratory are shown in Figure 3. These two heteroacids as well as the molybdate ion absorb very strongly in the ultraviolet region. The absorbance maxima of the α and β-silicomolybdic acids are at 329 and 339 nm respectively. The absorption curves of the two intersect at a wavelength of 341 nm, which is in good agreement with Strickland's (15) result. Between 341 nm and 480 nm, the absorptivity of the β-form is almost twice as great as that of the α-form.

Because of the very high absorptivity of both forms in the UV range, operating in this region for analytical purposes does seem beneficial. Indeed, De Sesa (19) suggested making measurements at 332 nm. Other authors (20, 21) reported optimum wavelength settings within the range of 370 - 425 nm. However, since the molybdate ion (See Figure 3) also absorbs very strongly in the wavelength region of 300 - 400 nm, it seems undesirable to make measurements below 400 nm because of the necessarily very high blank value.

In photometry, it is desirable to select a wavelength for measurement which is on a plateau of the spectral absorbance curve. Then slight changes in the wavelength setting will not significantly affect the measured absorbance. The slopes of the spectral curves of the α and β silicomolybdic acids are very steep in the wavelength region of 300 -

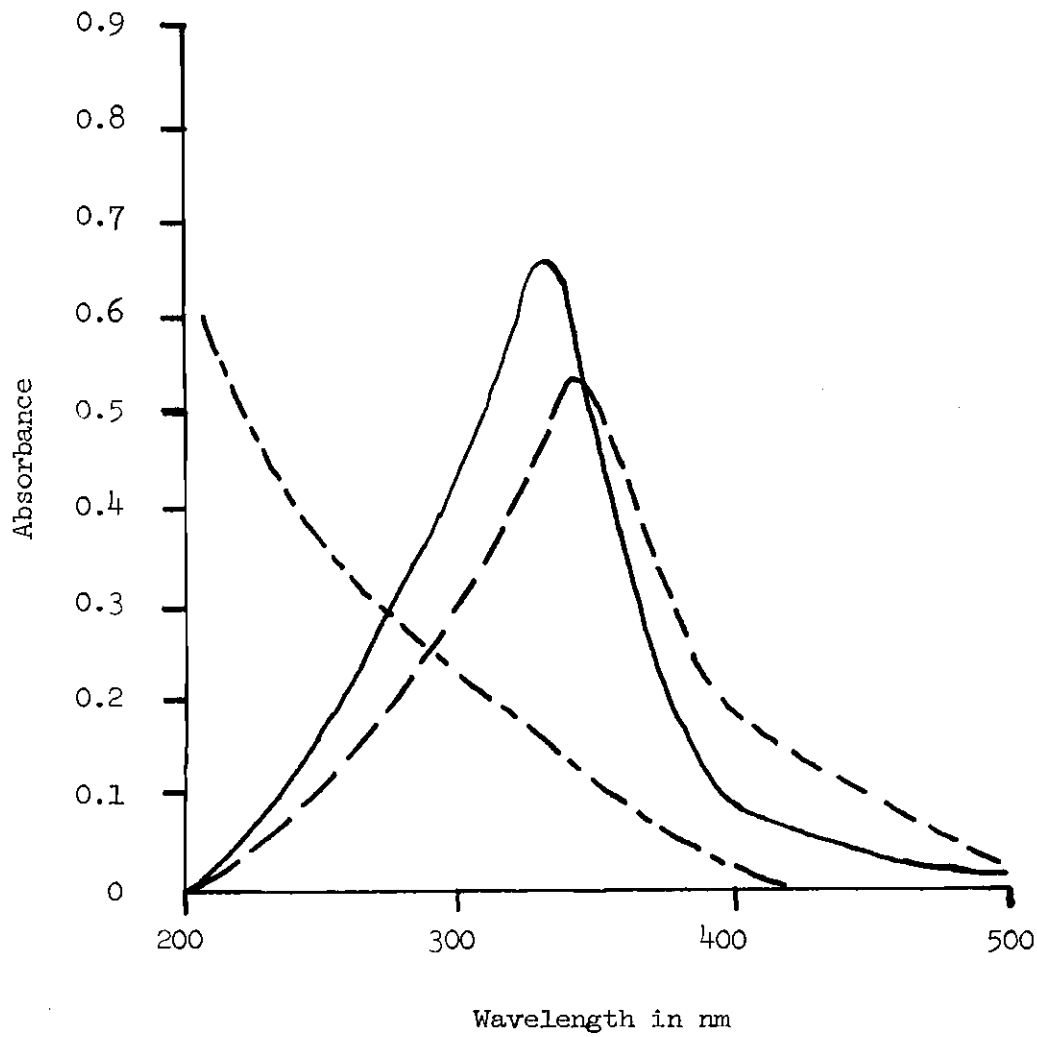


Figure 3. Spectral Curves of α and β Silicomolybdic Acid and the Molybdate Ion

Molybdate Ion (----)

α-Silicomolybdic Acid (——)

β-Silicomolybdic Acid (— — —)

400 nm. It is therefore undesirable to make measurements in this region. The obvious choice of the wavelength setting would be on the near plateau of the curve above 400 nm. Further, the blank value would be very low due to the low absorptivity of the molybdate ion. However, selecting this wavelength leads obviously to a tremendous loss in sensitivity. Consequently, a search for enhancing the absorptivity is of great practical importance, unless one wishes to turn to the highly sensitive modification of reducing to the heteropoly blue with all of its pitfalls and difficulties.

CHAPTER III

EQUIPMENT AND CHEMICALS

Laboratory Equipment

Spectrophotometers

All spectral curves were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer. All quantitative analytical absorbance measurements were made with a Bausch and Lomb Spectronic 20 spectrophotometer.

pH Meter

All pH measurements were made with a Corning Model 7 pH meter. This device was calibrated with Corning standard buffer of pH 7.00. The term pH in this work, refers to the pH measured with this instrument.

Glassware

The usual glassware such as beakers, flasks, separatory funnels, etc., were used as needed. For volumetric measurements class A volumetric glassware was used exclusively and without additional calibration.

Chemicals

Water

Deionized water was used exclusively.

Sodium Silicate

J. T. Baker reagent grade sodium meta-silicate was used. A standard 6.25×10^{-3} F silicate solution was prepared by dissolving 1.776 grams of sodium meta-silicate in water and diluting to exactly one liter with water. This concentration was accepted at face value without

further standardization.

Perchloric Acid

J. T. Baker "Analyzed" perchloric acid was used.

Sodium Hydroxide

Fisher certified standard sodium hydroxide was used.

Tartaric Acid

J. T. Baker reagent grade d - tartaric acid was used.

Sulfolane (Tetrahydrothiophene - 1, 1 - Dioxide)

Eastman Organic practical grade sulfolane was used. The sulfolane was purified by vacuum distillation at 118-121° at a pressure of 1.5 mm Hg. Vacuum distillation is necessary because sulfolane decomposes at temperatures well below its boiling point.

Storage of Solutions

All solutions were stored in polyethylene bottles.

CHAPTER IV

DESCRIPTION OF THE EXPERIMENTS

The use of sulfolane as an enhancing agent for photometric methods as described in Chapters I and II was applied to the silicomolybdic acid complex. Although the initial purpose of this investigation was to study the enhancing effect of sulfolane on the silicomolybdic acid complex, certain other advantages were discovered with the use of sulfolane. The scope of this work was greatly widened with the realization of these advantages.

Enhancement Studies

So far most authors have agreed that acetone is the best water-miscible enhancing agent for the silicomolybdic acid complex. The studies by Chalmers (8) and Halasz (9) were repeated in this laboratory for the α-silicomolybdic acid. While the enhancement effects were proven again, an observation was made that neither Chalmers nor Halasz reported, namely, the development of turbidity when operating in strongly acidic solutions. Investigations with sulfolane showed that this reagent has a greater enhancing effect (See Figure 4) and did not cause any turbidity. In addition, as mentioned previously, it is less volatile and thus seems to be overall, quite superior to acetone.

The color of the β-silicomolybdic acid is only slightly enhanced upon the addition of sulfolane. A possible explanation may be that in the strongly acidic solution necessary for the formation of this form,

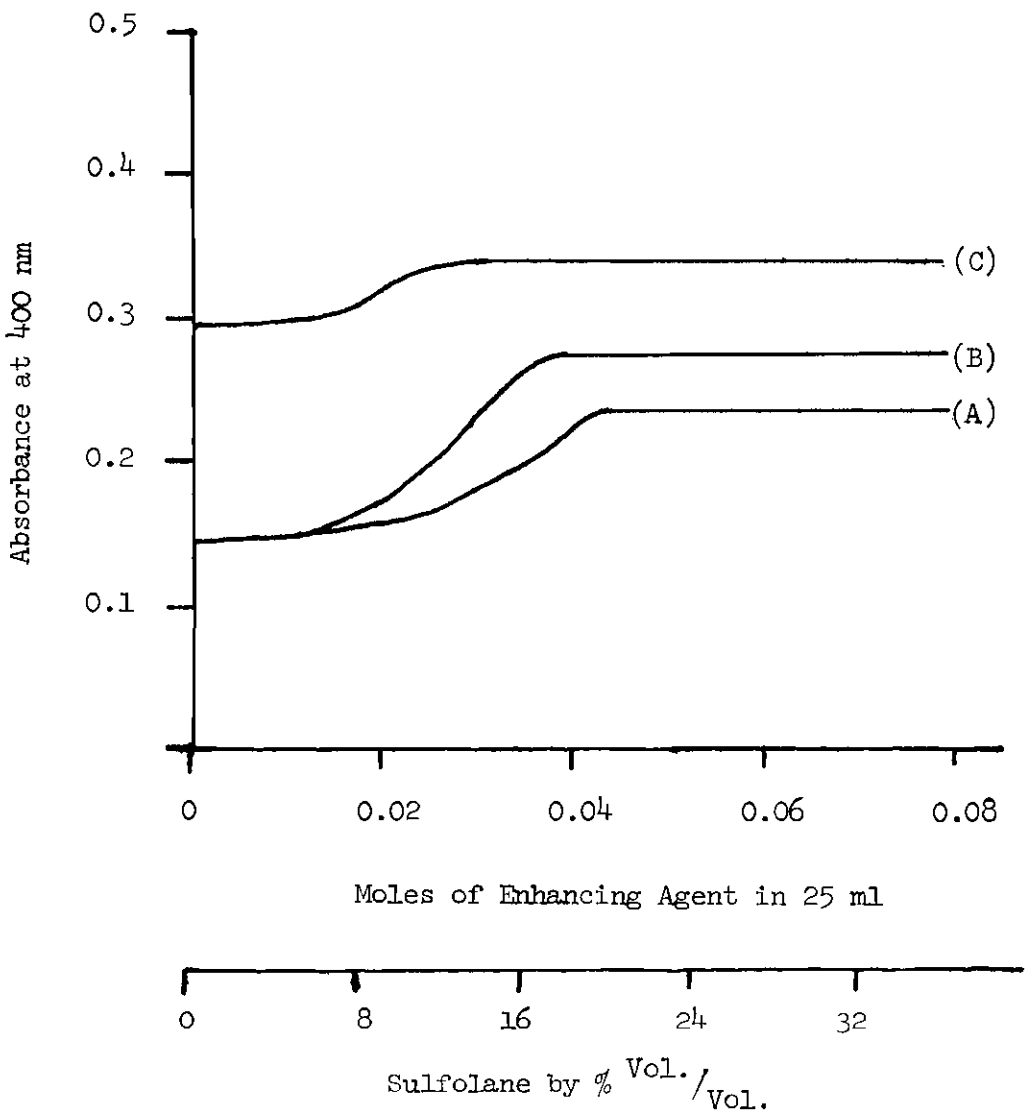


Figure 4. Enhancement Due to Additions of Sulfolane and Acetone

(A) α-Acid With Acetone

(B) α-Acid With Sulfolane

(C) β-Acid With Sulfolane

the water molecules in the hydration sheath are protonated and thus exchange with sulfolane is blocked.

The degree of enhancement for both forms (See Figure 4) increases with increasing concentration of sulfolane, but after a certain concentration is reached, the absorbance remains constant even upon further addition of sulfolane. The optimum concentration range for sulfolane is 20 to 40 percent volume by volume. Within this range, the absorptivity for both silicomolybdic acid forms is independent of the concentration of sulfolane and the amount of reagent added is not cirtical. At sulfolane concentrations higher than 40 percent V/V the solutions become intensely yellow due to the color enhancement of the excess molybdate ion by sulfolane. Analytical measurement under such conditions are not advisable because of the very high blank value.

Absorption Spectra

The absorption spectra (See Figure 5) of the α and β acid in the presence of sulfolane are very similar to the spectra of the α and β in the absence of the reagent (See Figure 3). Halasz (9) reported the absorbance maxima of the α-silicomolybdic acid to be 314 nm. The difference between this value and the 328 nm found in this laboratory is probably due to differences in the methods employed and the types of instruments used for measurement.

The absorbance maximum of the β-silicomolybdic acid in the presence of sulfolane is at 345 nm. This represents a 6nm upscale shift from the absorbance maximum with no sulfolane present. These shifts are in the same order of magnitude as reported by other authors for

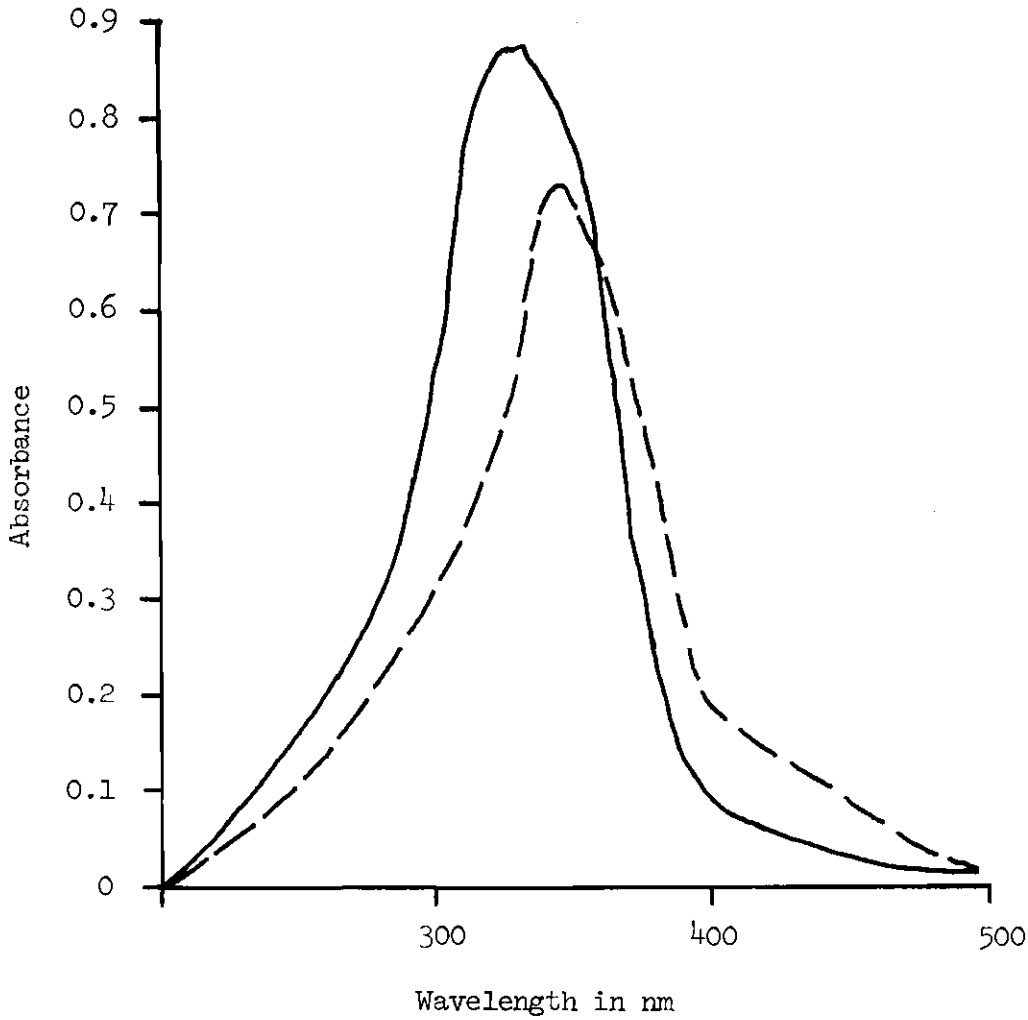


Figure 5. Spectral Curves for the Sulfolane - α and β Silicomolybdic Acids

Sulfolane - α Acid (———)

Sulfolane - β Acid (– – –)

various other water-miscible organic solvents.

Study of pH and Time Dependence

When operating within the pH range 2.5 to 3.9, the α-silicomolybdic acid forms exclusively and about 15 minutes are required for the reaction between the silicate and molybdate ions to go to completion. Further investigations showed that the α form is stable for at least several days. This stability is the reason why most procedures prefer operating with the α-form although the β-form has a much more favorable absorptivity.

When the reaction between silicate and molybdate ions takes place in solutions of a pH lower than 2, the stronger absorbing β-form results but immediately starts to convert to the α-form. The rate of this conversion depends on the pH, and cannot be controlled in a manner that would allow ready use of this form for analytical purposes.

When the influence of sulfolane on the two silicomolybdic acids was studied, a remarkable stabilization of the β-form was found, in addition to the enhancement of the absorptivity. In the presence of sulfolane, the β-silicomolybdic acid is stable over the pH range 0.1 to 1.8 (See Figure 6). Below pH 0.1 formation of the acid is incomplete and in solutions of a proton concentration greater than 0.3 m, no complex forms at all.

The stabilization of the β-form by sulfolane is effective, however, only at pH values below 2. When the solution is brought to pH 3 or higher, a rapid transformation of the sulfolane β-acid complex into the corresponding α-acid complex takes place. The latter complex then

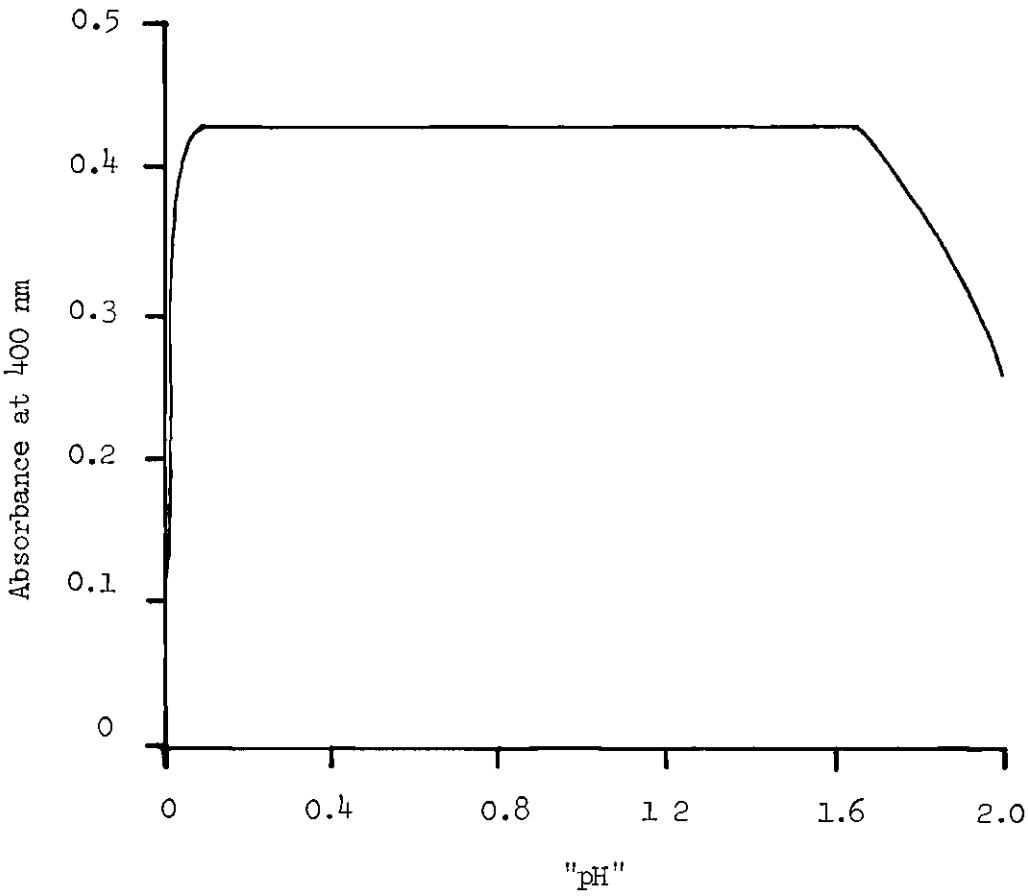


Figure 6. Graph of pH Versus Absorbance for the Sulfolane-8 Silicomolybdic Acid Complex

persists and does not change upon reacidification.

The stabilization of the β-form by sulfolane creates a new analytical possibility. Not only is the absorptivity of this form greater than that of the α-form (in absence as well as in presence of sulfolane) but operation in more strongly acidic medium has the added advantage of decreasing the number of interferences.

Interference Studies

Mellon (4) performed a rather exhaustive study of interferences in the heteropolymolybdate methods and gave maximum concentrations that could be tolerated for the various interfering ions. The investigation reported in this thesis was restricted to the most common interference, namely, the phosphate ion. Phosphate causes the greatest problem of all of the heteropoly acid forming ions.

Extractions were tested with the hope that a solvent could be found that extracts the heteropolyphosphate but not the heteropolysilicate or vice versa. However, within the short time at hand for the investigation, no positive results were obtained. It may well be questioned whether such a solvent exists at all.

Analytical methods make use of the fact that certain organic acids attack one heteropoly acid more than another. Chalmers (8) and others found that tartrate, citrate, oxalate, (and also mannitol) when present in large excess, rapidly attack the β-phosphomolybdic acid but react rather slowly with the corresponding silico compound. Tartrate was selected for further study because of its demonstrated success in rapidly displacing the phosphate from the molybdate while having no

effect on the β-silicomolybdic acid. Chalmers suggested that the tartrate and phosphomolybdate exist in a rapidly establishing equilibrium according to:

$$\text{Phosphomolybdate} + \text{Tartaric Acid} \rightleftarrows \text{Phosphate} + \text{Tartratomolybdate} \quad (3)$$

The equilibrium can be shifted to the right by adding an excess of tartaric acid.

The approach was investigated with regard to sulfolane containing complexes. As expected, the sulfolane - β - silicomolybdic acid remains unchanged in the presence of tartrate even when present in large excess. Unfortunately the sulfolane also stabilizes the β-phosphomolybdic acid which is decomposed to only a rather slight extent. Thus tartrate is of no use when working in the presence of sulfolane. Chalmers reported similar findings for the acetone - β - phosphomolybdic acid.

There is one possibility of solving the problem under certain circumstances. Use can be made of the difference in stability upon acidification. The sulfolane - β - silicomolybdic acid is completely decomposed in solutions containing a higher proton concentration than 0.3 M. In contrast, the corresponding phosphomolybdic acid complex is stable even in stronger acidic media. Thus, phosphate can be determined in the presence of silicate in one aliquot of the sample. In another aliquot, the sum of silicate and phosphate is determined and silicate obtained by difference. Of course, such a method poses severe restrictions as to the amounts absolute and relative of the two ions allowed.

Since the scope of the present investigation was limited, no further study of this possibility was made. The working procedure developed requires the restriction of phosphate definitely being absent.

Results

A calibration curve for the determination of unknowns was prepared from standard sodium silicate solutions (See Figure 7). The silicon was determined by the sulfolane - β - silicomolybdic acid method. The system obeyed Beer's Law for a silicon concentration up to 8 μg/ml. The sensitivity* is 0.5 μg/ml of silicon. The sensitivity of this method is considerably greater than Halasz's (9) reported value of approximately 2 μg/ml of silicon for the acetone - β - silicomolybdic acid method.

Determination of known amounts of silicon confirmed the practicability of the sulfolane - β - silicomolybdic acid method. Each unknown consisted of a measured volume of standard silicate solution. Some of the results of this series are shown in Table 1. The μg/ml of silicon as determined by the method are well within the realm of acceptable error.

Procedure

The following procedure was developed and, in many tests, proven to give the reliable results as reported in Table 1.

(1) Place the roughly neutralized sample solution containing up to 0.2 milligrams of silicon into a 25 - ml volumetric flask and add 4 ml of 0.3 F perchloric acid solution (NOTE 1).

(2) Add 5 ml of liquified sulfolane and 5 ml of 0.05 F ammonium

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* Here sensitivity relates to the slope of the calibration curve.

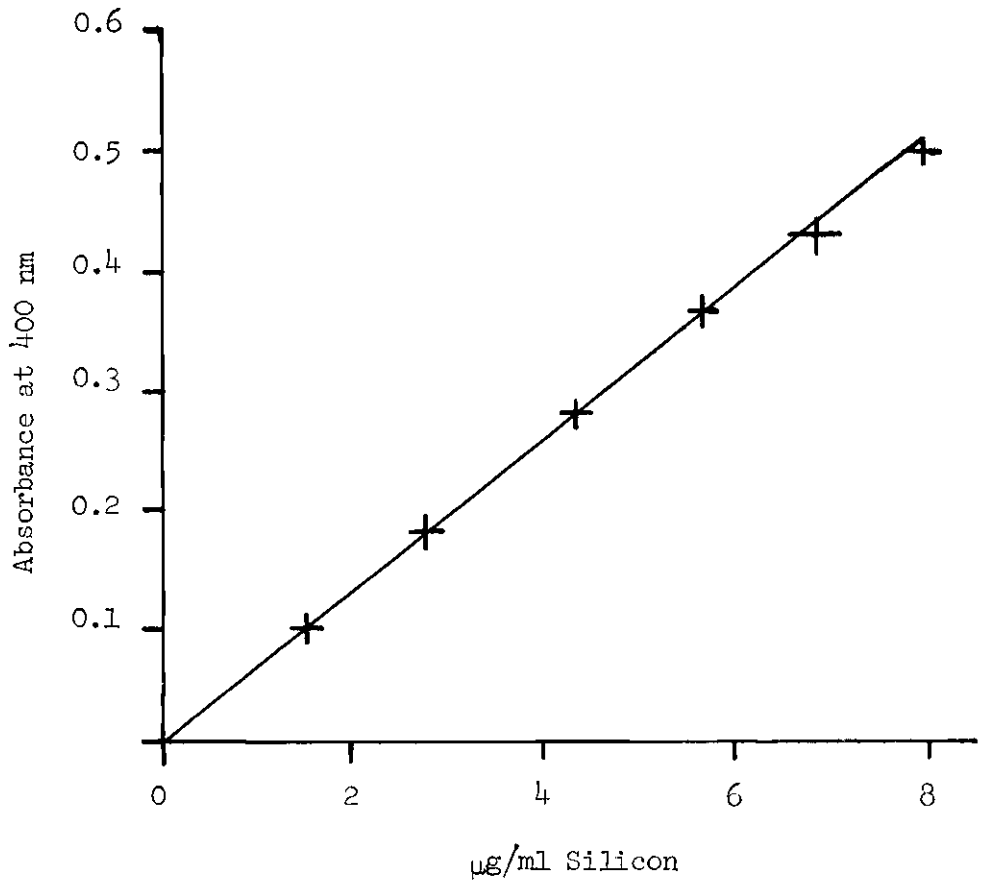

Figure 7. Calibration Curve for Silicon

From the Sulfolane-β-Silicomolybdic Acid Method

Table 1 Results of Silicon by the Sulfolane - β - Silicomolybdic Acid Method

μg/ml of Silicon		
Taken	Found	Δ
1.04	1.01	-0.03
1.38	1.34	-0.04
1.76	1.80	+0.04
2.07	2.06	+0.01
2.76	2.70	-0.06
2.90	2.96	+0.06
3.80	3.85	+0.05
4.14	4.05	-0.09
5.52	5.44	-0.08
6.90	6.84	-0.06

molybdate solution and dilute to mark with deionized water (NOTE 2).

(3) Allow the solution to stand for 15 minutes and then measure the absorbance at 400 nm versus a reagent blank. Obtain the result as usual from a calibration curve established by carrying known amounts of silicate through the procedure.

NOTES

1. The final pH of the solution at this point should be between 0.1 and 1.8.
2. Up to 10 ml of sulfolane can be added and the final molybdate concentration can vary from 0.005 to 0.01 F.

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